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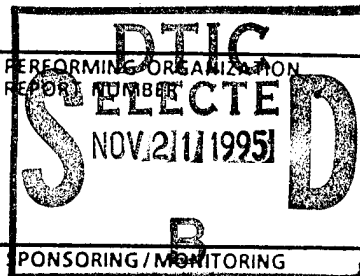
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Differences in the Self-Assembly of Thiol and Disulfide Derivatives of Viologens on Au

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Abstract

A direct comparison of the self-assembly on Au of thiol and disulfide derivatives of viologens bearing long n-alkyl chains was made in order to ascertain the relative efficiency of monolayer formation for each type of functionality. The structures the two derivatives which were studied can be written as $CH_3V^{2+}(CH_2)_{12}SH$ and $[CH_3V^{2+}(CH_2)_{12}S]_2$ for the thiol and disulfide, respectively, where V^{2+} represents the viologen (i.e. N,N'-dialkylated-4,4'-bipyridinium) redox group. In contrast to the behavior of n-alkyl thiols and di-n-alkyl disulfides, which adsorb to give very nearly the same surface coverage and interfacial properties, these two viologen derivatives exhibit markedly different saturation surface coverages for the fully formed monolayers of 1.8×10^{-10} mol cm^{-2} for the disulfide and 3.1×10^{-10} mol cm^{-2} for the thiol, as determined from the charge for exhaustive reduction and reoxidation of the viologen redox groups. In addition, monolayers with high surface coverages of the thiol derivative exhibited very sharply peaked cyclic voltammetric responses which are attributed to very strong interactions between the one-electron reduced cation radicals in the monolayer, a phenomenon which does not occur in monolayers prepared from pure samples of the disulfide derivatives. The accompanying paper describes a surface enhanced Raman study that suggests this interaction to be a type of radical dimerization. This unique electrochemical response is interpreted as resulting from a considerably more highly organized monolayer for the thiol derivative compared to the disulfide.

Introduction

The monolayers formed from spontaneous adsorption of several sulfur-containing functional groups onto Au, Ag, and Cu have attracted considerable attention both because they provide a facile entry into detailed studies of the relationship between structure and function at liquid/solid interfaces (1) and because of a range of potential applications. Examples include non-linear optical devices based on polar assemblies of various chromophores which can be produced with these methods by using the surface as a template (2), and the use of sulfur-based surface derivatization to produce surfaces with capabilities for chemical sensing (3). In all such studies, the structural characteristics of the monolayer are of paramount importance, given that the gross arrangement, orientation, accessibility, mutual interactions, etc. of the molecules within the surface film will be determined in large measure by the geometry and density of the adsorbate bonds to the surface, the shapes of the adsorbates, and the consequent interfacial topology.

Perhaps the two most common sulfur-containing functional groups for providing anchors to these metal surfaces are the thiol and disulfide groups. Bain et al. (4,5) have studied the mode of bonding to the surface (via XPS in the S(2p) region) for both alkyl thiol and dialkyl disulfide derived monolayers, as well as the contact angles formed between such monolayers and water or hexadecane. They concluded that the monolayers produced from these two precursors are very nearly the same, exhibiting virtually identical XPS spectra (indicative of identical modes of surface bonding). Only very subtle differences were observed between monolayers derived from thiols and disulfides, which were manifested in slightly lower contact angles for the disulfide monolayers. More recently, Lamp et al. (6) have used ellipsometry, IRRAS (infrared reflection absorption spectroscopy), contact angles, and electrochemical desorption measurements to critically compare the monolayers formed from thiols and disulfides. They, too, find only very subtle, but detectable, differences between these two types of monolayers. In contrast to these reports that alkyl thiols and dialkyl disulfides form monolayers with discernibly different properties, Hickman et al. (7) examined the formal potentials and saturation surface coverages of monolayers derived from alkyl thiol and dialkyl disulfide

derivatives of ferrocene and reported identical behavior with respect to these two parameters. Thus, the issue of whether the behavior of thiol-derived and disulfide-derived monolayers can be expected to behave identically remains unresolved.

Our group (8,9) has studied the electroactive monolayers formed by spontaneous adsorption on Au of viologen derivatives of the general formula $CH_3(CH_2)_nV^{2+}(CH_2)_mSH$, where n ranges from 0 to 17, m ranges from 3 to 16, and V^{2+} represents the viologen (i.e. N,N'-dialkylated-4,4'-bipyridinium) redox group. We have recently discovered that the synthetic route which we had employed to produce these compounds actually gave a mixture of the thiol and disulfide derivatives (of general formula $[CH_3(CH_2)_nV^{2+}(CH_2)_mS]_2$). Variability of the saturation surface coverages for the monolayers formed from these mixtures prompted us to carefully examine the self-assembly of pure samples of the thiol and disulfide derivatives, which is the topic of this contribution. During the course of this study, we observed striking cyclic voltammetric (CV) signatures due to what we believe to be very strong interactions between the one-electron reduced viologen cation radicals for the high surface coverage thiol monolayers. As will be discussed below, the appearance of this signature is a very sensitive function of the surface coverage, with only the highest (i.e. near saturation) coverages showing this behavior. In the accompanying paper, we describe some surface enhanced Raman spectroscopy (SERS) experiments that strongly suggest these interactions are due to formation of π complex dimers between the open shell planar radicals in the monolayer. Given the fairly unusual nature of these dimers, it is worthwhile to briefly discuss what is known about this phenomenon. A more detailed discussion is given in the accompanying paper.

Hausser and Murrell (10) were the first to report dimerization of open shell, radical forms of planar aromatic species. Kosower made extensive studies of the dimers formed from the one electron reduced radicals of several planar aromatic systems, including the pyridinium derivatives (11). In general, these dimers are formed by virtue of overlap of the singly occupied (in the radicals) π^* orbitals of adjacent ring systems when in a face-to-face orientation. The orbital interaction

generally leads to mixing of the π^* states, leading to spectral shifts in the π-π^* transitions, as well as the appearance of a new, lower energy peak due to the transition between the two new states derived from mixing of the π^* levels.

In many of the cases studied, dimerization is encouraged by linking the two interacting ring systems at both ends of a propyl chain to provide for the proper orientation and ring-ring distance. (This is a ground state equivalent of the n=3 rule in photochemistry (12), which states that maximal interaction of the open shell, excited states of planar conjugated systems occurs when the ring systems are linked with a propyl spacer (i.e. Ar-$(CH_2)_3$-Ar, where Ar is a planar ring system.) For example, Kosower and Itoh (13) used the characteristic spectroscopic features described above to study the π complex dimers formed after reduction of several n=3 pyridinium derivatives.

In addition to spectral manifestations of the formation of the π complex, there are also effects on the electrochemical behavior of these species. In particular, the reduction potential for production of the radical is generally shifted to less negative potentials when dimer formation is possible. This effect has been observed for n=3 pyridinium derivatives (14) and for n=3 viologen derivatives (15), and the shifts have been used to calculate the equilibrium constants for dimerization. As will be seen below, the thiol-derived viologen monolayers described here appear to exhibit these same features (shifted formal potentials due to dimerization) when the viologens are present at very high surface coverages, while the disulfide-derived monolayers, which give lower saturation surface coverages, do not.

Experimental

Synthesis. Bis[N-methyl-N'-(12-dodecyl)-4,4'-bipyridinium] disulfide diiodide dibromide ([1V12S]$_2$). (See Scheme 1) Methyl iodide was reacted with 4,4'-dipyridyl in a 0.9 to 1 mole ratio for 3 h in acetone at reflux. The precipitate was collected and washed with acetone 3 times to remove unreacted starting materials. NMR revealed pure N-methyl-4,4'-bipyridinium iodide which was reacted with a 5 molar excess of 1,12-dibromododecane for

3 days in acetonitrile. The precipitate was collected, washed 3 times with acetonitrile, and characterized by NMR. The terminal bromide of the purified product was reacted with a 5 molar excess of thiourea in water. After 3 days the reaction was stopped and solvent was removed by rotary evaporation. The product (thiouronium salt) was washed with acetone to remove excess thiourea and characterized by NMR. The thiouronium salt was cleaved to the thiol by refluxing in a 1.0 to 0.9 mole ratio of thiouronium salt to bicarbonate for 4 h in DMF under nitrogen. Upon completion, 10% HCl was added dropwise until a slightly acidic pH was achieved, then the solvents were removed. 1HNMR (DMSO, ppm); 9.42(d, bipyridyl, 4 H); 9.34(d, bipyridyl, 4 H); 8.82(m, bipyridyl, 8 H); 4.70(t, methylene next to N, 4 H); 4.47(s, methyl next to N, 6 H); 2.68(t, methylene next to S, 4 H); 1.98(m, methylene beta to N, 4 H); 1.60 (m, methylene beta to S, 4 H); 1.26(m, rest of methylenes, 32 H).

N-methyl-N'-(12-mercaptododecyl)-4,4'-bipyridinium iodide bromide (1V12SH). (See Scheme 1) 12-bromo-1-dodecyl thioacetate (prepared from the corresponding alcohol(5)) was reacted with N-methyl-4,4'-bipyridinium iodide (prepared as discussed above) in a 1:1 mole ratio in DMF under nitrogen for 36 h at 120 °C. The product was washed with acetonitrile 3 times and characterized by NMR. To obtain the thiol, the thioacetate of the product was dissolved in 50 ml of dry cold degassed methanol. 5 ml of acetylchloride was added while stirring and the mixture was warmed to room temperature. The solution was reacted for 3 h under nitrogen purge. The solvents were then removed to leave pure 1V12SH. 1HNMR (DMSO, ppm); 9.42(d, bipyridyl, 2 H); 9.34(d, bipyridyl, 2 H); 8.82(m, bipyridyl, 4 H); 4.70(t, methylene next to N, 2 H); 4.47(s, methyl next to N, 3 H); 2.50(q, methylene next to S, 2 H); 2.20(t, SH, 1 H); 1.96(m, methylene beta to N, 2 H); 1.50 (m, methylene beta to S, 2 H); 1.2 to 1.4(m, rest of methylenes, 16 H).

Unambiguous differentiation between the thiol and disulfide derivatives is achieved by NMR by virtue of the position of the CH_2 protons next to S (at 2.68 and 2.50 ppm for the disulfide and thiol derivatives, respectively) and by the direct observation of the thiol proton as a triplet centered at 2.20 ppm in perdeuterated DMSO.

Instrumentation and Electrode Preparation. A standard H-cell was used for all electrochemical experiments and cleaned in hot nitric acid for 12 h prior to use. A SSCE was used as the reference electrode and isolated from the rest of the cell using a glass frit. All potentials are reported with respect to this reference electrode. The counter electrode was a platinum wire. The thin film gold working electrode was prepared by derivatizing a 2.54 cm diameter quartz crystal with 3-mercaptopropyl trimethoxysilane as described by Majda (16) and vapor depositing 150 nm of Au with an Edwards Coating System (E306A) at a rate of 0.1 nm/s. The electrochemically active area of the keyhole pattern Au electrode was 0.34 cm^2 with an effective surface roughness of 1.2 measured with Au oxide stripping by the method of Schultze (17). All surface coverages are corrected for this roughness. This value of surface roughness is in reasonable agreement with the value expected based on past reports of the roughness of vapor deposited thin film Au electrodes (18).

Ion Exchange Procedure. The counter ions of the cationic viologen derivatives were exchanged to alleviate problems of competitive specific adsorption on gold from the iodide and bromide counter ions that are present from the synthesis. Nitrate was chosen as the counter ion because the viologen nitrate salts are water soluble and nitrate is not strongly adsorbed to Au. The nitrate form was obtained in two different ways, either by use of an ion exchange column (Dowex 1-8X) or by metathesis from saturated solutions. Either method worked equally well but the metathesis procedure was used most frequently due to its simplicity. For this procedure, the viologen was precipitated as the hexafluorophosphate salt (V(PF$_6$)$_2$) in water by mixing a concentrated solution of NaPF$_6$ and a saturated solution of viologen. The nitrate form was subsequently prepared by dissolving V(PF$_6$)$_2$ in acetone and precipitating V(NO$_3$)$_2$ by addition of an acetone solution of tetrabutylammonium nitrate.

Monolayer Preparation. The general procedure for monolayer preparation was to expose the Au electrode to a solution of the appropriate viologen derivative dissolved in 0.1 M aqueous supporting electrolyte (either NaCl, NaClO$_4$, or NaNO$_3$). The viologen disulfide monolayers were coated from 0.5

mM solutions (which is close to the saturation limit), while the thiols (which are considerably more soluble) were coated from 1 mM solutions. To monitor the progress of monolayer formation, the coating solution was removed periodically and the monolayer was rinsed with 95% ethanol and/or DI water, folllowed by cyclic voltammetric evaluation of the surface coverage in pure supporting electrolyte. This coating/evaluation procedure was repeated until the surface coverage had reached a constant value and the electrochemical behavior became invariant. The Au surface was typically exposed to the coating solution for ca. 24 hours during this procedure.

Chemicals. All chemicals used in synthesis and electrochemical experiments were of reagent grade or better. Water was purified by a Millipore purification train and was used for all electrolyte solutions.

Results

Figure 1 shows the cyclic voltammogram (CV) of a monolayer of $[CH_3V^{2+}(CH_2)_{12}S]_2$ (hereafter abbreviated as $[1V12S]_2$) at saturation coverage. The two redox couples which are observed at -0.38 and -0.85 V are due to the two, reversible one-electron reductions which are characteristic of monolayers formed from these viologen derivatives (8,9). These redox couples are illustrated in Equation 1.

$$V^{2+} + e^- \rightleftharpoons V^+ + e^- \rightleftharpoons V^0 \qquad (1)$$

The saturation surface coverage (Γ_{sat}) for this disulfide derivative is 1.8 x 10^{-10} mol cm^{-2}. This value is considerably lower than those we have previously reported for similar viologen derivatives (8,9). The discrepancy can be traced to the fact that the earlier samples were comprised of mixtures of thiols and disulfides. Given the much more rapid kinetics of thiol compared to disulfide adsorption (4) and the higher saturation surface coverages for the thiols (see below), we suspect that the earlier Γ_{sat} values were consistently higher than the present value for this disulfide derivative due to the presence of thiols in the earlier samples.

Figure 2 shows the CV of $CH_3V^{2+}(CH_2)_{12}SH$ (hereafter abbreviated as 1V12SH) at saturation surface coverage. There are several salient features

of this voltammogram. First, there are sharply peaked anodic and cathodic responses which appear at ca. -0.3 V, on the positive side of the wave for the first redox couple. Second, there are similar sharply peaked responses in the second wave which are less well-defined. Third, the Γ_{sat} value for this thiol derivative is 3.1 x 10^{-10} mol cm^{-2}, considerably larger than that for the disulfide derivative given above. In addition we have observed that the ratio of the relative charge of the sharp peak to the broader wave for the first redox couple is a very sensitive function of the surface coverage, with the ratio increasing steeply as Γ_{sat} is approached. For a given monolayer this ratio is not dependent on scan rate between 0.01 and 1.0 V s^{-1}. We propose that this sharply peaked response is due to the formation of π complex dimers of the cation radicals within the monolayer. SERS data on these monolayers, which are presented in the accompanying paper (19), reveal that the intensities of Raman peaks which have been previously attributed to viologen dimers (20-22) track the charge under the sharp peaks, in support of this interpretation of the electrochemical data.

The dependence of this dimerization process on surface coverage can also be demonstrated by preparing a monolayer of the thiol derivative and then diluting (by displacing some of) the viologens in the monolayer via exposure to a solution of n-dodecyl thiol, a strategy originally employed by Chidsey et al. (23) to reduce lateral interactions between ferrocene moieties in a self-assembled monolayer. Figure 3 shows the result of such an experiment. Curve A is the CV of a monolayer of 1V12SH at Γ_{sat} which exhibits the characteristic π complex dimer response. Curve B is the CV of the same monolayer after a 30 minute exposure to a 1 mM solution of n-dodecyl thiol in ethanol. The loss of viologen from the surface due to displacement is evident from the smaller charge under Curve B than Curve A (by ca. a factor of 2). In addition, the sharp peak which is characteristic of the dimer is completely absent in Curve B, indicating that the decrease in surface coverage leads to loss of the π complex interaction between adjacent cation radicals, presumably due to the larger average separation between them and an overall lower degree of congestion within the monolayer.

Discussion

The data described above clearly show that the thiol and disulfide viologen derivatives studied here spontaneously adsorb onto Au electrodes to give quite different saturation surface coverages. They also show that unique interadsorbate interactions exist between viologen groups in these monolayers which occur only at relatively high surface coverages of the viologen group (i.e. only in the thiol case). Two questions arise from consideration of these results. First, why are the Γ_{sat} values so different for the thiol and disulfide viologen derivatives, especially in comparison to the virtually identical values obtained for n-alkyl thiols and dialkyl disulfides (4,5) and for the ferrocene thiol and disulfide derivatives for which a direct comparison has also been made (7)? Second, what is the origin of the marked dependence of dimer formation on the viologen surface coverage?

Past work has demonstrated that the kinetics of production of close-packed monolayers from thiols and disulfides are quite different, with the thiols exhibiting faster kinetics by between a factor of 10 and 100 (4,5). The origin of this difference has been attributed to the larger size of the disulfides (which is aggravated by the relatively large C-S-S-C dihedral angle of ca. 90° (24)) which inhibits approach of the disulfide from solution through the monolayer to reach the metallic surface. This inhibition is expected to become increasingly important as the surface population increases. However, for the alkyl thiols and dialkyl disulfides which have been previously studied (4,5), as well as the ferrocene thiol and disulfide derivatives (7), these steric constraints have not been sufficient to lead to significantly different saturation coverages provided that sufficient time is allowed for the monolayer to form.

We suspect that in the present case the origin of the significantly different Γ_{sat} values for 1V12SH and [1V12S]$_2$ is due to a combination of factors. First, the steric bulk of the viologen group is considerably larger than that of either an alkyl chain or a ferrocene group, especially when one considers that each doubly charged viologen group which enters the monolayer brings with it two anionic counterions (nitrate anions in the present case), a fact which is confirmed by direct observation of loss of these counterions during reduction of the viologen groups within the

monolayer (8,9). Thus, not only are the steric bulk and large dihedral angle of the disulfide working against the attainment of high saturation coverages, but so is the steric bulk of the pendent redox group. This would be expected to be especially severe for $[1V12S]_2$ compared to 1V12SH, since the former must accomodate two such groups, while the latter need only accomodate one. Second, the dicationic charge of the viologen group must cause considerable electrostatic repulsion between the partially formed monolayer and any incoming molecules. Again, this would lead to a greater barrier for entry into the monolayer for $[1V12S]_2$ compared to 1V12SH, due to their respective 4+ and 2+ charges. This effect should be somewhat mitigated at higher ionic strengths due to better electrostatic screening. It is worth noting in this regard that we have found assembly of these monolayers to occur more rapidly in solutions of high (ca. 0.1 M) ionic strength than at low ionic strength. Thus, both the considerable steric bulk of the viologen group and its relatively high charge appear to lead to inhibition of the self-assembly process, with these effects being most pronounced for the disulfide derivative.

Turning now to the issue of the origin of the strong surface coverage dependence of the dimerization process, we first briefly compare the present results with those of other groups who have studied monolayers of non-covalently anchored viologens present at electrode surfaces. Cotton and coworkers (21,25) have studied monolayers and multilayers of several viologens using electrochemistry and SERS. In no case have they observed electrochemical signatures of dimerization, although they have observed SERS bands which could be attributed to dimerization in monolayers of $CH_3V^+(CH_2)_{15}CH_3$ (21). Kaifer and coworkers (26-29) and Widrig and Majda (18) have also used electrochemistry to study physically adsorbed monolayers of long chain viologen derivatives without any indication of dimerization in the electrochemical responses of their systems. Bunding-Lee (30) examined the monolayers formed from long chain dialkyl sulfide (as opposed to dialkyl disulfide) viologen derivatives, again with no indication of dimerization in the electrochemical response. The only previous reports of double peaked CV's which could be indicative of dimerization in viologen monolayers are by us (8,9) for a monolayer formed from a mixture of $[10V10S]_2$ and 10V10SH, and by Lee and Bard (31) for

Langmuir-Blodgett (LB) films of a long chain viologen derivative. Dilution of the viologen in the LB film with arachidic acid led to loss of the dimer response, in behavior analogous to that shown in Figure 3. The model used by them to explain the double peaked CV's was one in which the predominant interaction was assumed to be between V^{2+} and V^{+}, rather than between two V^{+}'s (as would be the case for the π complex dimers we describe here), and was based on the results of a statistical mechanical treatment [32] of ordered arrays of redox groups rather than on a direct spectroscopic observation as in the present case. We favor the interpretation in which the sharp features in the CV's are assumed to arise from dimerization of two V^{+}'s [19], because this model is consistent with a large body of previous spectroscopic work.

The two previous reports of dimerization were for viologen monolayers which share two features with the thiol-derived monolayers described here. First, the surface coverages are all quite high, very near to the geometrical limit for close-packing of viologens oriented with the long axis of the ring system perpendicular to the plane of the surface. Second, the viologen groups are held in place fairly rigidly, either by virtue of covalent attachment to the underlying electrode or by virtue of immobilization within a LB film. Saturation surface coverages for various types of viologen monolayers have been reported by several workers. The range of experimental values for cases in which Γ_{sat} is thought to be determined by close-packing of the viologen groups is ca. (3.1 - 3.7) x 10^{-10} mol cm^{-2} [9,18,28,31]. These values are reasonably close to the estimation of Γ_{sat} ((3.7 - 4.3) x 10^{-10} mol cm^2) based on the size of the viologen group, which is 38-45 $Å^2$ depending on whether the counterions are included (and what their identity is) and whether the excluded area per ring system is assumed to be only the projected area or the cylinder defined by free rotation of the ring system about its long axis [9,18]. Since many of the previous studies on non-covalently bound viologens have reported Γ_{sat} values in this range, but no electrochemical evidence for dimerization, it appears that close proximity is necessary, but not sufficient, for the observation of this phenomenon. Thus, in our and Lee and Bard's cases, there must be an additional factor(s) which promotes the π complex interaction. Possibilities include higher degrees of order (i.e.

the viologen groups are more highly oriented and/or are oriented in the proper way for π complexation) and lack of dynamic behavior (i.e. the viologen groups are unable to diffuse laterally and/or undergo exchange with the solution phase) of the viologen groups within the LB and covalently attached monolayers. The orientation of the viologen groups in these thiol- and disulfide-derived monolayers is currently being evaluated by SERS and IRRAS to aid in interpreting these results. These results (33) suggest an orientation in which the long axis of the viologen ring system is roughly parallel to the surface normal, which would be consistent with the discussion above.

Conclusions

The primary conclusion of this study is that the self-assembly of thiol and disulfide viologen derivatives does not produce saturated monolayers with the same surface coverages and electrochemical behavior. The lower saturation surface coverage of the disulfide derivative is probably due to a combination of the relative bulkiness of the disulfide compared to the thiol, a size difference that is probably exacerbated by the relatively large dihedral angle of the C-S-S-C bonds, and to the considerably more unfavorable electrostatics of approach and insertion into the monolayer of the tetracationic disulfide compared to the dicationic thiol. Once the monolayer is partially formed, access to the underlying Au surface is probably much more restricted for the disulfide than for the thiol, leading to a higher saturation surface coverage and a consequently more highly organized monolayer for the thiol. We speculate that the electrochemical response which has been attributed to the π-complexed dimer is due to a higher degree of organization and smaller molecular area for the viologens in the thiol monolayers which lead to an increased probability that the cation radicals can approach to the proper distance and enter into the proper orientation for overlap of the π^* orbitals on adjacent cation radicals to produce the dimer. Thus, it seems that in the present case the presence or absence of the electrochemical signature of the π-complexed dimer functions as a fairly sensitive measure of the degree of organization and interadsorbate spacing for the redox groups which are pendent from the anchored alkyl chains.

It is still unclear exactly what determines the relative amount of monomer and π-complexed dimer for the monolayers that have different surface coverages. One possibility that seems likely is that it is simply a measure of the fraction of the viologens in the monolayer that have the proper orientation and/or conformation (i.e. the proper geometrical relationship) for dimerization. Thus, at lower surface coverages where the viologen groups are, on average, farther apart from one another, the likelihood that any two viologens will be in close enough proximity to dimerize is expected to be lower than at higher surface coverages. We return to this point in the accompanying paper (19) on a Raman spectroscopic study of the π-complexed dimers in these monolayers.

The finding that thiols and disulfides which have large and/or highly charged pendent groups have different tendencies toward self-assembly is of quite general interest given the considerable effort being expended both in fundamental studies of the n-alkyl thiol and di-n-alkyl disulfide systems and in using sulfur anchors on Au, Ag, or Cu for purposes of constructing molecular assemblies with unique and controllable properties. The important point here is that disulfide systems which bear large and/or highly charged pendent groups may not assemble to give as highly organized an assembly or as high a surface coverage as do the corresponding thiol systems. Thus, considerable care is called for in the design of systems of this type, especially when control over the detailed structural features of the monolayer is necessary for the application in mind.

Acknowledgement

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Figure Captions

1. CV of [1V12S]$_2$ monolayer at saturation coverage of $\Gamma = 1.8 \times 10^{-10}$ mol cm^{-2} in 0.1 M NaNO$_3$, scan rate = 100 mV s^{-1}.

2. CV of 1V12SH monolayer at saturation coverage of $\Gamma = 3.1 \times 10^{-10}$ mol cm^{-2} in 0.1 M NaNO$_3$, scan rate = 100 mV s^{-1}.

3. A) CV of 1V12SH monolayer, $\Gamma = 2.8 \times 10^{-10}$ mol cm^{-2}. B) CV of monolayer from A after exposure to a 1 mM solution of n-dodecylthiol in air-saturated ethanol for 30 min., = 1.35 $\times 10^{-10}$ mol cm^{-2}. For both scans scan rate = 100 mV s^{-1} and supporting electrolyte = 0.1 M NaClO$_4$.

Current, μA

Potential V vs SSCE